

1015,217



## PATENT SPECIFICATION

NO DRAWINGS

1015,217

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## COMPLETE SPECIFICATION

## Self-Extinguishing Resins containing Free Radical Initiators

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to self-extinguishing resins and methods for their preparation. More particularly the invention concerns the enhancement of the flameproofing properties of an alkenyl aromatic polymer containing a halide by the admixture therewith of a free radical initiator such as sulfenamides, hydrazones, organic disulfides,  $\alpha, \alpha'$ -diphenyl- $\alpha$ -methoxybibenzyl, azo compounds or quinone imines.

Halides are sometimes added to alkenyl aromatic resins such as polystyrene to make them self-extinguishing, i.e., incapable of sustaining a flame for more than a few seconds when the flame used to ignite the resin is removed. The halides most often used for this purpose are chlorinated and brominated organic compounds although inorganic compounds such as ammonium bromide are sometimes used. Although the desired flameproofing characteristics may be obtained with these agents, it is necessary in some instances to use substantial quantities of the halide to obtain the desired self-extinguishing properties. These high concentrations of halide may introduce any of several undesirable properties in the resin. For example, the halide often dilutes or plasticizes the resin thereby reducing physical properties such as tensile

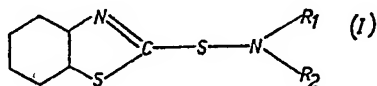
strength and heat distortion temperature. Another property commonly affected is the color of the resin, particularly after exposure to elevated temperature or actinic light owing to the poor thermal and photo-chemical stability of the halides. Also, severe corrosion of molding equipment is frequently experienced with resins containing halides having poor thermal stability. Some halides impart a musty odor to the resin when used at high concentrations. To avoid these undesirable effects of the halide the quantity used is often that which provides the minimum required flameproofing properties.

It has now been found that the self-extinguishing properties of the halide can be enhanced substantially by the use of a free radical initiator such as the hydrazones, organic disulfides,  $\alpha, \alpha'$ -diphenyl- $\alpha$ -methoxybibenzyl, azo compounds, quinone imines or sulfenamides in combination with the halide whereby a lesser amount of the flameproofing agent may be employed without sacrificing self-extinguishing properties.

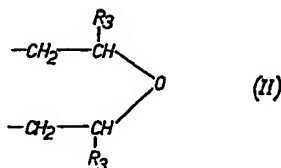
The sulfenamides which are delayed action vulcanization accelerators as characterized by the plot of Mooney viscosity against time are those which are particularly useful as adjuvants for self-extinguishing polymers containing halides as flameproofing agents. Thus, N-cyclohexyl-2-benzothiazole sulfenamide, as well as other sulfenamides having a cure time of about 50 percent or more of N-cyclohexyl-2-benzothiazole sulfenamide when present in the same concentration in a similar unvulcanized rubber formulation have been found to be effective adjuvants for self-extinguishing resins.

The sulfenamides which have been found

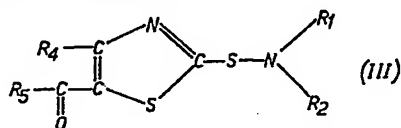
to be most particularly effective in flameproofing alkenyl aromatic resins have the general formula:



- 5 where  $R_1$  is hydrogen, an alkyl, cycloalkyl or a phenyl group;  $R_2$  is an alkyl, cycloalkyl, phenyl, or the mercaptobenzothiazole group, or where  $R_1$  and  $R_2$  collectively are



- 10 where  $R_3$  is hydrogen or an alkyl group; as well as the corresponding sulfenamides represented by the general formula



- 15 where  $R_4$  is an alkyl group and  $R_5$  is an alkyl or alkoxy group.

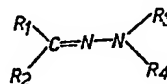
- Formula (I) includes compounds such as N - *tert.* - butyl - 2 - benzothiazole sulfenamide; N - cyclohexyl - 2 - benzothiazole sulfenamide; N,N - diethyl - 2 - benzothiazole sulfenamide; N - isopropyl bis(2 - benzothiazole sulfenamide); N,N - dicyclohexyl - 2 - benzothiazole sulfenamide; and N - phenyl - 2 - benzothiazole sulfenamide. Examples of sulfenamides represented by formula (II) are: N - oxydiethylene - benzothiazole - 2 - sulfenamide and 2,4 - dimethyl - 3 - oxypentamethylene - benzothiazole - 2 - sulfenamide. Formula (III) includes sulfenamides such as 5 - carbomethoxy - 4 - methyl - 2 - thiazole N - isopropyl sulfenamide and 5 - acetyl - 4 - methyl - 2 - thiazole N - *tert.*butyl sulfenamide.

- Among the disulfides which have been found to be effective adjuvants are benzyl disulfide, xylyl disulfide, butylxanthic disulfide, benzothiazole disulfide, as well as polydisulfides such as dithio bis(*p* - *tert.* - amylphenol disulfide).

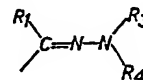
- These disulfides have been used in the past as chain transfer agents in the polymerization of styrene to prevent the formation of extremely long polymer chains, thereby producing lower molecular weight polymers. The relative effectiveness of these agents has been designated as the transfer constant in styrene polymerization, with those agents having the

higher constants being the more effective. These transfer constants are discussed by C. Walling, "Free Radicals in Solution," John Wiley & Sons, New York (1957) pages 148—160. In general the disulfides having transfer constants greater than about 0.6 at 50° C. are especially suitable adjuvants for the flameproofing halides. However, disulfides having transfer constants of less than 0.6 may be employed, as illustrated by benzyl disulfide which has a coefficient of only 0.03 at 50° C. yet enhances the flameproofing properties of the halides.

The hydrazones which have been found to be particularly effective in this invention may be represented by the formula



wherein  $R_1$  represents an alkyl, aryl, or aralkyl radical,  $R_2$  represents an alkyl, aryl or aralkyl radical or a hydrazone group having the formula



$R_3$  represents hydrogen or an alkyl, aryl or aralkyl radical and  $R_4$  represents an aryl, aralkyl or halogenated aryl radical. These hydrazones are the type which may be produced by the reaction of a ketone with a phenylhydrazine. Examples of hydrazones covered by this general formula are those which may be obtained by reacting phenylhydrazine with acetone, methyl ethyl ketone, diethyl ketone, methyl propyl ketone, acetophenone, benzophenone and hexanonephenone as well as diketones such as 2,3 - pentadione having adjacent carbonyl groups. In addition to phenyl hydrazines, suitable adjuvants may be prepared from 2,5 - dichlorophenylhydrazine and 1,1 - diphenyl hydrazine.

Among the suitable azo compounds are azobisisobutyronitrile, azobiscyclohexanenitrile and the azonitrile from cyclobutanone. Suitable quinone imines include *p*-quinone dioxine, *p*-dibenzoylquinone dioxine, 2,6-dichloroquinone chlorimide and N - chloro - *p* - benzoquinone imine.

The utility of these compounds in enhancing the self-extinguishing properties of resins was demonstrated in a series of tests. The resin used in these tests was polystyrene. The flameproofing agents were intimately mixed with the resin by dissolving the materials in methyl chloride then rapidly evaporating the solvent thereby producing a foamed structure. Test bars approximately 1/4 inch (6.35

mm.) thick by 1/2 inch (12.7 mm.) wide and 3—5 inches (7.6—12.7 cm.) long were cut from the foamed polymer for the burning tests. The self-extinguishing properties were determined by holding one end of the bar in the flame of a micro-burner for four seconds then withdrawing it from the flame and noting the length of time required for the flame to extinguish. The results of these tests are listed in Table I. The self-extinguishing times (S.E.) reported are the averages of several observed values where multiple tests were made. The halide used in preparing these samples was acetylene tetrabromide (ATB). The concentrations of both the free radical initiator and the ATB are expressed as parts per 100 parts of resin (phr).

TABLE I

EFFECT OF VARIOUS FREE RADICAL INITIATORS ON SELF-EXTINGUISHING TIME OF POLYSTYRENE CONTAINING ACETYLENE TETRABROMIDE

Free Radical Initiator	phr	ATB phr	S.E. Time seconds
None		2.5	Burns
None		3.0	8
N- <i>tert.</i> -butyl-2-benzothiazole sulfenamide	1	2	1.4
N-cyclohexyl-2-benzothiazole sulfenamide	1	2	1.6
N-isopropyl bis(2-benzothiazole sulfen)-amide	1	2	2.8
N- <i>tert.</i> -butyl bis (2-benzothiazole sulfen)-amide	1	2	1.0
N-oxydiethylene-benzothiazole-2-sulfenamide	1	2	2.4
2,4-Dimethyl-3-oxapentamethylene benzothiazole-2-sulfenamide	1	2	2.3
2-propanone phenylhydrazone	1	2	<1
2-butanone phenylhydrazone	1	2	5
2-pentanone phenylhydrazone	1	2	4.6
acetophenone phenylhydrazone	1	2	4.6
benzophenone phenylhydrazone	1	2	4.2
2-propanone 1-methyl-1-phenylhydrazone	0.5	1	11
acetophenone 1-methyl-1-phenylhydrazone	0.5	2	<1
benzophenone 1-methyl-1-phenylhydrazone	1	2	5
2-propanone 1,1-diphenylhydrazone	0.5	1	11
acetophenone 1,1-diphenylhydrazone	0.5	1	2.8
benzophenone 1,1-diphenylhydrazone	1	2	2.4
xylyl disulfide	1	2	2
benzothiazole disulfide	1	2	2.1
butylxanthic disulfide	1	2	1.2
benzyl disulfide	1	2	6.6

TABLE I (cont'd.)

EFFECT OF VARIOUS FREE RADICAL INITIATORS ON SELF-EXTINGUISHING TIME OF  
POLYSTYRENE CONTAINING ACETYLENE TETRABROMIDE

Free Radical Initiator	phr	ATB phr	S.E. Time seconds
dithio bis( <i>p-tert.</i> -amylphenol disulfide)	2	2	<1
Poly( <i>p-tert.</i> -amylphenol disulfide)	1	2	1.8
$\alpha,\alpha$ -diphenyl- $\alpha$ -methoxybibenzyl	1	1	<1
azobiscyclohexanenitrile	1	2	2
<i>p</i> -quinone dioxine	1	2	1.2
<i>p</i> -dibenzoylquinone dioxine	1	2	1.4
2,6-dichloroquinone chlorimide	1	2	<1

5 From these data it can be seen that polystyrene containing 2.5 parts ATB without a free radical initiator of this invention is not self-extinguishing whereas polymer containing only 2 percent ATB in the presence of 1 percent free radical initiator has a low S.E. time.

10 The polydisulfide appearing last in the table is similar to the one immediately above it, the difference being that the former contains more *p-tert.*-amylphenol groups in the molecule than the latter. A molecule of the dithio bis(*p-tert.*-amylphenol disulfide) contains four of these groups connected by three disulfide linkages whereas the poly(*p-tert.*-amylphenol disulfide) contains more than four of these groups connected by disulfide linkages.

20 These adjuvants are also effective in molded solid resins. Test bars were made by grinding the foamed resin then compression molding

the powder at 140—148° C. for 1.5 minutes. Bars prepared in this manner which contained 2 phr ATB and no adjuvant were not self-extinguishing whereas bars containing only 1 phr ATB in combination with 1 phr of *N-tert.* - butyl - 2 - benzothiazole sulfenamide extinguished in 14 seconds.

30 The flameproofing properties of halides other than ATB in combination with the free radical initiators were investigated using foamed polystyrene test bars prepared in the same manner as described above. The results of these further tests are listed in Table II. As in Table I, the concentrations of the flameproofing agents are listed in phr and the self-extinguishing times are the averages of several tests. These data illustrate the ability of the free radical initiators to enhance the self-extinguishing properties of various halides commonly used to prepare flameproof resins.

TABLE II

SELF-EXTINGUISHING PROPERTIES OF POLYSTYRENE CONTAINING A FREE RADICAL  
INITIATOR AND VARIOUS HALIDES

Halide	phr	Initiator	phr	S.E. Time Seconds
Dibromotetrachloroethane	2.0	None		8.0
"	1.5	A	0.5	3.6
"	1.0	D	1.0	3.0
"	1.5	C	0.5	2.4
Pentabromomonochlorocyclohexane	2.0	none		Burns
"	1.5	A	0.5	3.0
"	1.5	B	0.5	3.2
"	1.5	C	0.5	5.8
"	1.0	D	1.0	2.4
"	1.0	E	1.0	<1.0
Tris(2,3-dibromopropyl) phosphate	4.0	none		Burns
"	2.0	none		>25
"	3.0	A	1.0	3.6
"	3.0	C	1.0	1.8
"	2.0	D	2.0	2.8
"	1.0	E	1.0	8.0
Tetrachloroethane	12.0	none		Burns
"	10.0	B	2.0	8.0
"	10.0	C	2.0	3.4
Tris(dichloropropyl) phosphate	15.0	none		Burns
"	13.0	A	2.0	4.8
"	13.0	B	2.0	5.8
"	13.0	C	2.0	1.0
"	10.0	D	2.0	1.8
Hexachloroethane	12.0	none		Burns
"	10.0	B	2.0	3.2
"	10	D	2.0	3.0

TABLE II (cont'd.)

Halide	phr	Initiator	phr	S.E. Time Seconds
Hexachlorobenzene	12	none		Burns
"	10	B	2.0	5.0
Hexabromobenzene	4.0	none		Burns
"	2.0	D	2.0	12
Pentachloroethane	12.0	none		Burns
"	10.0	D	2.0	7.8

A = *N-tert*-butyl-2-benzothiazole sulfenamide

B = *N-tert*-butyl bis(2-benzothiazole sulfen)amide

C = poly(*p-tert*-amylphenol disulfide)

D = 2-propanone phenylhydrazone

E =  $\alpha,\alpha'$ -diphenyl- $\alpha$ -methoxybibenzyl

- 5 In addition to the halides listed in the above table, these adjuvants may be used to enhance the flameproofing properties of other halides such as ammonium bromide, 2,2-bis[3,5 - dibromo - 4 - (2,3,3 - tribromo-  
10 alloxy)phenyl]propane, bis(2,3,3 - tribromo-allyl)maleate, and 2,3,3 - tribromoallyl 2,4,6-tribromophenyl ether.
- 10 These unique combinations of flameproofing agents may be used with homopolymers and copolymers of alkylene aromatic monomers such as styrene,  $\alpha$ -methylstyrene, ethylstyrene, isopropyl styrene, *tert*-butylstyrene, vinyl  
15 xylene, and chlorostyrene. This invention may

also be used to advantage with copolymers containing principally styrene with minor amounts of other monomers as well as with the high impact type styrene polymers containing about 2—20 weight percent of a  
20 rubbery polymer such as polybutadiene, polyisoprene, or a butadiene-styrene elastomer such as GR—S. Table III represents data on the flameproofing properties of a number of these resins containing acetylene tetrabromide  
25 in combination with various free radical initiators. The combinations of these agents are expressed in the same units as in Tables I and II.

TABLE III

SELF-EXTINGUISHING PROPERTIES OF ALKENYL AROMATIC RESINS CONTAINING  
ACETYLENE TETRABROMIDE AND A FREE RADICAL INITIATOR

Resin	ATB phr	Free Radical Initiator	phr	S.E. Time Seconds
Polystyrene — 79 percent styrene, 21 percent $\alpha$ -methylstyrene	8	None		15.0
„	6	A	2	8.0
„	6	B	2	5.6
„	6	C	2	3.0
„	6	E	2	1.0
Polystyrene — 93 percent styrene, 7 percent acrylonitrile	4	none		13.6
„	3	A	1	1.8
„	3	C	1	<1.0
„	4	D	1	3.8
Polystyrene Containing 5 percent GR—S	4	none		19
„	3	A	1	7
„	3	B	1	12
„	2	D	1	12.0
„	5	None		6
Polystyrene Containing 5 percent GR—S	4	C	1	2
„	3	None		>25
„	2	E	1	15
„	2	E	2	10
Polyvinyltoluene	8	None		Burns
„	6	B	2	15
„	6	C	2	12
„	6	D	2	4.2

A = N-*tert*-butyl bis(2-benzothiazole sulfen)amide

B = N-*isopropyl* bis(2-benzothiazole sulfen)amide

C = acetone phenylhydrazone

D = poly(*p-tert*-amylphenol disulfide)

E =  $\alpha$ ,  $\alpha'$ -diphenyl- $\alpha$ -methoxybibenzyl

- Other tests were made wherein the flame-proofing agents were present in the emulsion during suspension polymerization of the styrene monomer in laboratory bottle polymerization apparatus. The polymer beads produced in this manner were water-washed then devolatilized in a vacuum oven at 25 mm. and 80° C. for 16 hours. Compression molded standard test bars 6" x 1/2" x 1/8", were tested for self-extinguishing properties according to the Underwriter's Subject No. 94 Test. The results of these tests are presented in Table IV. As in Table I the concentrations are in weight percent.
- The Underwriter's Subject No. 94 Test is carried out as follows:—
- The test specimen is supported from the upper end, with the longest dimension vertical, by a clamp on a ring stand so that the lower end of the specimen is 3/8 inch above the top of a burner tube. The burner is then placed remote from the sample, ignited, and adjusted to produce a blue flame 3/4 inch in height.
- The test flame is placed centrally under the lower end of the test specimen and allowed to remain for 10 seconds. The test flame is then withdrawn, and the duration of flaming or glowing combustion of the specimen is noted. If flaming or glowing combustion ceases within 30 seconds after removal of the test flame, the test flame is again placed under the specimen for 10 seconds immediately after flaming or glowing combustion of the specimen stops. The test flame is again withdrawn

and the duration of flaming or glowing combustion of the specimen noted.

If the specimen drips flaming particles or droplets while burning in this test, these drippings shall be allowed to fall onto a horizontal layer of cotton fibers (untreated surgical cotton) placed 1 ft. below the test specimen. Significantly flaming particles are considered to be those capable of igniting the cotton fibers.

The duration of flaming or glowing combustion of vertical specimens after application of the test flame, average of three specimens (6 flame applications) shall not exceed 25 seconds (maximum more than 30 seconds) and the portion of the specimen outside the clamp shall not be completely burned in the test.

Materials which comply with the above requirements and do not drip any flaming particles or droplets during the burning test will classify as "Self-Extinguishing, Group I."

Materials which comply with the above requirements, but drip flaming particles or droplets which burn only briefly during the test will classify as "Self-Extinguishing, Group II."

Similar results were obtained employing N - tert - butyl bis(2 - benzothiazole sulfen)-amide. This technique is not employed to advantage with compounds such as the hydrazones which generally inhibit the polymerization of alkenyl aromatic compounds.

TABLE IV

EFFECT OF  $\alpha,\alpha'$ -DIPHENYL- $\alpha$ -METHOXYBIBENZYL ON ADDITIVES IN POLYSTYRENE

S.E. Additive	percent	Synergist, percent	S.E. Time, Sec.
Bis(2,3,3-tetribromoallyl)maleate	3.0	0	23, >25
"	3.0	1.0	0,0
"	1.5	1.0	0,0
"	0.75	1.0	2,0
"	0.38	0.5	2,10
2,4,6-tribromophenylacrylate	8.0	0	>25
"	8.0	1.0	4,4
Tetrachlorodibromoethane	1.0	0	>25
"	1.0	0.5	2
"	0.5	1.0	3



- Another technique which may be used to obtain an intimate mixture of the resin and flameproofing agents is that of pressurization. According to this method, about 100 parts by weight of polymer granules are placed in about 150 parts by weight of an aqueous solution which may contain a suspending agent, e.g., one weight percent methyl cellulose. The self-extinguishing agents and about 2–10 weight percent of a blowing agent such as normal pentane, if a foamable resin is desired, are also added to the slurry which is then placed in a pressure vessel where it is agitated and heated to a temperature of 90–130° C. over a period of 15–45 minutes. The slurry temperature is held at that level for a period up to four hours then gradually lowered to the initial starting temperature so that granules will not foam when the reactor is opened. The polymer is separated from the slurry and washed to remove suspending agent and other materials coating the granules. This method has been found to be effective in impregnating the granules with from 70 to 95 or greater percent of the self-extinguishing agents which are added to the slurry.
- Table V lists self-extinguishing times for polystyrene which was flameproofed in this manner. The halide used in these samples was acetylene tetrabromide (ATB). The pressurization time does not include the warm-up and cooling times.

TABLE V  
POLYSTYRENE FLAMEPROOFED BY PRESSURIZATION

Free Radical Initiator	phr	ATB phr	Pressurization		S.E. Time seconds
			Temp. °C.	Time—Hr.	
None		3	95	3	Burns
None		4	95	3	10
N- <i>tert.</i> -butyl-2-benzothiazole sulfenamide	2	2	95	1	2.6
„	2	2	95	4	4.2
„	2	2	105	3	4.8
„	2	2	130	0	3.6
N- <i>isopropyl</i> bis(2-benzothiazole sulfen)amide	2	2	95	4	3.5
N- <i>tert.</i> -butyl bis(2-benzothiazole sulfen)amide	2	2	95	4	3.8
Acetone phenylhydrazone	1	1.5	95	0	6.4
„	1	1.5	95	1	3.2
„	1	1.5	95	3	1.8
„	2	1.5	130	3	5
Dithiobis( <i>p-tert.</i> -amylphenol disulfide)	2	2	95	4	4.8
Poly ( <i>p-tert.</i> -amylphenol disulfide)	2	2	130	1.5	1.0
Benzyl disulfide	2	2	95	1	1.8
„	2	2	130	0.5	6.2

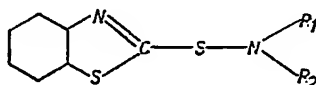
The concentration of halide necessary to obtain the desired flameproofing properties depends to a great extent on the particular halide used as illustrated in Table II. Additionally, some resins require a higher concentration of flameproofing agents than others as shown in Table III. The free radical initiators are advantageously employed in amounts of from 0.1 to 3.0 parts per hundred parts of resin. More than 3.0 parts per hundred may be employed if desired but is generally not economically justifiable. Most advantageously one employs from 0.5 to 2.0 parts per hundred parts of resin. The amount of a particular synergist employed will vary with the amount and kind of halide used.

#### WHAT WE CLAIM IS:—

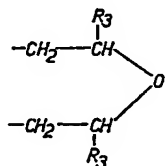
1. Alkenyl aromatic polymer composition which contains a halogen flameproofing agent characterized in that it also contains a free radical initiator which is a sulfenamide, a hydrazone, an organic disulfide, an azo compound, a quinone imine or  $\alpha,\alpha$ -diphenyl- $\alpha$ -methoxybibenzyl as a flameproofing adjuvant.

2. Composition of Claim 1 wherein the free initiator is N - cyclohexyl - 2 - benzothiazole sulfenamide or a sulfenamide which produces a cure time in the vulcanization of rubber of at least 50 percent of the cure time for a similar formulation containing the same concentration of N - cyclohexyl - 2 - benzothiazole sulfenamide.

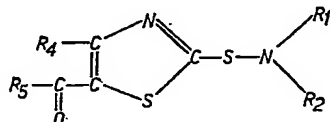
3. Composition of Claims 1 or 2 wherein the sulfenamide has the formula:



where  $R_1$  is hydrogen, an alkyl, cycloalkyl or phenyl group;  $R_2$  is an alkyl, cycloalkyl, phenyl or the mercaptobenzothiazole group, or where  $R_1$  and  $R_2$  collectively are



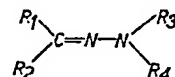
where  $R_3$  is hydrogen or an alkyl group, or the formula:



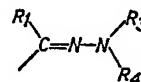
where  $R_4$  is an alkyl group and  $R_5$  is an alkyl or an alkoxy group.

4. Composition of Claims 1 to 3 wherein the sulfenamide is N - *tert.* - butyl - 2 - benzothiazole sulfenamide, or N - *tert.* - butyl bis(2 - benzothiazole sulfen)amide.

5. Composition of Claim 1 wherein the free radical initiator is a hydrazone having the formula:



wherein  $R_1$  represents an alkyl, aryl, or aralkyl radical;  $R_2$  represents an alkyl, aryl, or aralkyl radical or a hydrazone group having the formula:



$R_3$  is hydrogen or an alkyl, aryl, or aralkyl radical; and  $R_4$  is an aryl, aralkyl, or a halogenated aryl radical.

6. Composition of Claim 5 wherein the hydrazone is 2-propanone phenylhydrazone, 2,3 - pentanedione bis - phenylhydrazone, or phenone 1 - methyl - 1 - phenylhydrazone, or acetophenone 1,1 - diphenylhydrazone.

7. Composition of Claim 1 wherein the free radical initiator is benzyl disulfide or an organic disulfide having a transfer constant in styrene polymerization greater than about 0.6.

8. Composition of Claim 7 wherein the disulfide is benzothiazyl disulfide, butylxanthic disulfide, xylyl disulfide, or poly (*p* - *tert.* - amyl - phenol disulfide) containing at least 4 *p* - *tert.* - amylphenol groups in the molecule.

9. Composition of Claims 1 to 8 which contains from 0.1 to 3.0 parts of free radical initiator per hundred parts of composition.

10. Process for improving the self-extinguishing properties of an alkenyl aromatic resin comprising intimately incorporating in said resin a halogen flameproofing agent and 0.1 to 3.0 parts per hundred of a free radical initiator which is a sulfenamide, a hydrazone, an organic disulfide, an azo compound, a quinone imine, or  $\alpha,\alpha$ -diphenyl- $\alpha$ -methoxybibenzyl.

11. Process for making self-extinguishing alkenyl aromatic resins comprising: preparing an aqueous dispersion of resin granules together with flameproofing agents consisting of a self-extinguishing quantity of a halogen flameproofing agent and from 0.1 to 3 parts per hundred parts resin of a free radical initiator which is a sulfenamide, a hydrazone, an organic disulfide, an azo compound, a quinone imine, or  $\alpha,\alpha$ -methoxybibenzyl, agitating the dispersion while gradually increasing the temperature

thereof to a level in the range 90 to 130° C., maintaining the temperature level for a period up to 4 hours, thereafter gradually decreasing the temperature of the dispersion to approximately ambient temperature, then recovering said self-extinguishing resin granules therefrom.

12. Process for improving the flameproofing characteristics of an alkenyl aromatic polymer containing a halogenated compound wherein the polymer is produced by the suspension polymerization of an alkenyl aromatic monomer in the presence of the halogenated compound, which comprises the addition of a synergistic quantity of  $\alpha, \alpha'$ -diphenyl -  $\alpha$ -methoxybibenzyl to the suspension during the polymerization, the quantity of said  $\alpha, \alpha'$ -diphenyl -  $\alpha$ -methoxy - bibenzyl being equal

to from about 0.1 to about 2.0 weight percent of said polymer.

13. Polymer composition according to claim 1 containing a halogen flameproofing agent and a free radical initiator substantially as hereinbefore described.

14. Process according to claim 10 for improving the self-extinguishing characteristics of alkenyl aromatic polymers substantially as hereinbefore described.

15. Alkenyl aromatic polymer compositions whenever prepared by the process claimed in any one of claims 10, 11, 12 or 14.

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